



Lead-acid battery model for the derivation of Peukert's law

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Abstract

In this paper a survey is given of the pros and cons of the existing models for the lead-acid battery. Next, a diffusion model is proposed which explains inter alia the occurrence of sharp lead sulfate walls observed earlier by Haeblér et al. The model also leads to an expression similar to Peukert's law. Finally, in order to account for secondary effects in the lead sulfate distribution the model has been extended to include a second internal diffusion mechanism. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

During the past 50 years considerable effort has been applied to the search for lead-acid battery models. Due to the extreme complexity of this type of battery, it has been impossible to find one single model that adequately describes its behaviour. In fact, one has the impression that research on lead-acid batteries can continue for several more decades. In the past battery models have been developed for several purposes:

Type (a) models. These have been developed to gain a better understanding of the physical, chemical and electrical phenomena involved in the charge/discharge process of an electrochemical cell. These models can take into account the porous character of the plates, the reaction rates of the different components, the plate dilatation. Examples of such models can be found in [1–5,16].

Type (b) models. For the prediction of external electrical parameters during a stationary charge or discharge regime: the voltage-time curve, the variation of

the internal resistance during discharge and the decrease of the apparent capacity with discharge current (Peukert's law, [13], p. 173). Some authors combine semi-empirical data such as Peukert's law, diffusion equations and electrical equivalent circuits in the models [5–7,21], whereas others use a system approach [8] in which the battery is considered to be an electrical system with two connections and non-linear voltage-current characteristics. A number of these models are summarised and discussed in [9].

Type (c) models. In order to describe the dynamic behaviour of a cell during operation, electrical equivalent circuits have been proposed in which double layer and diffusion phenomena are emulated with lumped capacitors and resistors [10]. The need for good and accurate dynamic models arose from the application of lead-acid cells in stand-alone photovoltaic systems. Since the charge regime depends on insolation and the discharge regime of the consumer, both can be very irregular in a practical situation. The same applies to the batteries used in electric vehicles where the discharge operation is irregular [11]. Dynamic models were mainly developed in order to have a means for predicting the state-of-charge under such a **solicitation** of the battery. Advances obtained in the type-a models

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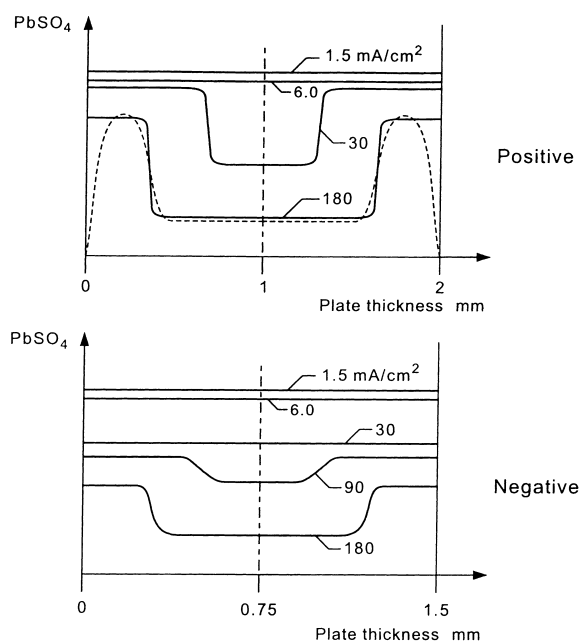


Fig. 1. Schematic representations of the lead sulfate distributions obtained by Haebler et al. [3,12] for the negative and positive plates and for different discharge current densities. The dotted curve represents an experimentally obtained lead sulfate distribution. The solid curves are the idealised shapes.

also influence the construction of type (b) and (c) models.

By studying references on modelling one can see that the older models were based on the search for analytical solutions of the diffusion equation combined with an electrical circuit. More recent models heavily rely on the solution of similar equation sets by means of digital simulation. The latter permits us to study a large range of the parameters involved. The disadvantage, however, is that the results have to be accepted more or less blindly, while their contribution to a better understanding of the phenomena is minimal. Moreover, since the number of parameters to be estimated is large, the temptation exists to force the parameters in a direction that gives the best results without the certainty that this corresponds with physical reality. For example, the expression used in the Shepherd model [18] for the description of voltage during a charge or discharge contains a parameter 'internal resistance' which can be negative if derived from real voltage curves. As is the case for the design of integrated electronic circuits, such calculations should better be used for the optimisation of parameters after a suitable model has been found and compared with reality.

The model we propose here belongs to category (a) and its purpose is to explain the lead sulfate profiles that occur under different discharge current density

conditions in the plates of a lead-acid cell. These curves are shown in [12] and were obtained by Bode, Haebler, Panesar and Voss by means of X-ray microprobes. Fig. 1 shows a schematic representation of these results. It is important to note that these lead sulfate distributions have been determined at different current levels and for 0, 25, 50 and 100% depth-of-discharge. The differences between the negative and positive plate will be disregarded. In the literature, the explanation of these profiles is rather descriptive. For example, it is accepted that a discharge starts at the orifice of the pores in the plates and that it progresses into the pores. The penetration depth is either diffusion- or current-limited [12], depending on the current density. Once the pores are completely covered at their surfaces, sulfate ions diffuse through the surface lead sulfate layer. At large current densities acid diffusion limits the discharge process and the acid in the deeper part of the pores becomes exhausted [7]. Although some of the computer models produce lead sulfate distributions [5,7], it seems that they differ considerably from those obtained experimentally by Bode et al. None of the models sufficiently explains all of the following obvious characteristics of the lead sulfate profiles of Fig. 1.

1. The relatively flat lead sulfate levels for the inner and outer zones of the plates for high current densities. The flat shape is more pronounced for the discharged positive than for the negative plate. One has to admit that this effect is not always so pronounced. In [7] measurements demonstrate that the lead sulfate profile can depend on the position of the measurement probe, probably due to electrode inhomogeneity.
2. The remarkably steep shape of the curve in the transition zone between a high and a low lead sulfate level is shown in the figures of [12]. Therefore, we will call this lead sulfate profile a 'wall'. It has to be noticed that one can presume that the actual shapes are steeper than those shown by the measurements because these results are distorted by the finite probe resolution. This can be deduced from the fact that at the plate surface, the lead sulfate level rises over a finite length from zero to the constant level, instead of having the same level at the plate surface. However, a lower lead sulfate level may also be caused by the higher current density at the surface of the plate [7].
3. The position of the wall is related to the current density.
4. The lead sulfate levels between the two walls are flat and depend on the discharge current density. At first sight one could suppose that, once the internal pore acid is depleted, this level should remain constant and not depend on the discharge current density. Since this is not the case there must exist some

extra diffusion of acid from the volume surrounding the pore.

Our purpose is to show how Peukert's equation follows from the diffusion limited lead sulfate model, or at least how a comparable formula can be determined. In order to comply with the observation that the central lead sulfate level is current dependent we will also introduce a second diffusion mechanism.

2. Pore model

The model we present below resembles the classical cylindrical pore model with some modifications. Computer models such as found in [5] are very complicated because they take into account the acid flow due to pore shrinking, varying porosity and acid concentration, the variation of the polarisation resistance with the depth-of-discharge. A clear insight into the time behaviour of such a system cannot be gained because the important parameters such as acid concentration (C) and the conductivity σ are continuously changing during discharge.

It has to be remarked that modelling by means of lumped or distributed resistances and conductances, and applying electrical network laws for the plate material, e.g. node equations, can only represent a faint reflection of reality. Especially for pasted plates the deviations can be expected to be large, due to the following complications.

1. Individual particles are good conductors (lead, lead dioxide) or bad conductors (sulfate, expander). In a partially charged cell, a mixture of both exists.
2. Electrical conduction is extremely complicated. It is accepted that a plate consists of a conducting skeleton that surrounds the pores [22,23]. The skeleton also mechanically supports the active mass. But, conductive particles can be in contact with conducting or badly conducting particles. In the first case, current can easily skip from one particle to another. In the second case, current has to flow from one conducting particle to another through the acid.
3. Particles can entirely be surrounded by lead sulfate and never be charged or discharged.
4. Sulfation and the occurrence of different lead sulfates complicate the conduction mechanism ([13], p. 188).
5. The plate continuously changes its structure during a cycle and the actual behaviour of a cell is therefore only an average effect.
6. The actual potentials in the neighbourhood of particles with such an irregular shape can never be calculated.

The pore model with an analytical solution can there-

fore only be an average and poor model for the plates. It has, however, the merit to give a better understanding of the fundamental problems involved than a pure computer simulation. In the pore model we here propose we will demonstrate that the potential drop in the longitudinal direction of the pore is almost negligible and that during a constant current discharge lead sulfate is formed almost everywhere at the pore surface. At this place it is appropriate to remember the accepted view about pores. In general the pores are classified into two classes: the macropores or transport pores (larger than $0.05\ \mu\text{m}$) and the micropores (smaller than $0.05\ \mu\text{m}$) [23,12]. The macropores are the basic transport ways along which the flow of ions and water move between the internal region of the plate and the external acid reservoir. Macropores form the largest part of the pore volume. Micropores provide the surface upon which the electrochemical reactions take place [22,12]. The pore model therefore is built up of a cylindrical tube with micropores connected to its surface. The simplifications we adapt for our model are well known: the pore cross section is constant, no structural changes (volume changes due to material transformation) or dilution of the acid due to the fixation of the sulfate ions occurs during the discharge, no influence of expanders, potentials in the pore are replaced by their average values [1] and the system is homogeneous in space. This permits one to reduce the system to a one- or two-dimensional system.

Models such as [2] or [19] suggest that the sulfation starts at the orifice of the pore and progresses into longitudinal direction [17]. This effect is here considered to be temporary (start of discharge) and it is therefore neglected. The fast voltage drop at the start of discharge of a fully charged cell is a manifestation of this phenomenon: the very small initial pore resistance becomes considerable once the whole pore surface is covered with the initial layer of lead sulfate. Our model will only be valid for the next phase, i.e. the constant voltage plateau during the discharge.

It will be shown that the pore model we developed leads to a new solution of the diffusion equation and a capacity limiting law.

2.1. Current distribution in a pore

It is common to introduce the following parameters for a cylindrical pore: average pore diameter a , average pore length L' , tortuosity T . The tortuosity causes a total length $L = L'T$ of the pores. Since the exact field equations inside the pore are difficult to solve, we simplify the problem by supposing that the pore behaves as a cylindrical conductor with a slightly isolated internal surface. The isolation is caused by lead sulfate that is formed immediately after the discharge starts. Initially the current is the largest at the pore orifice

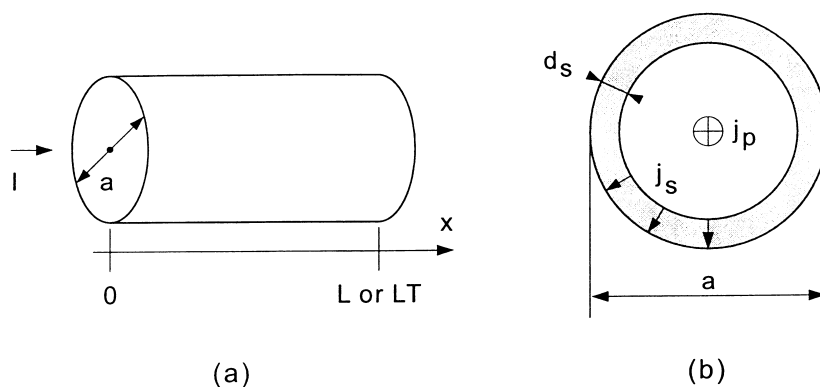


Fig. 2. Ideal cylindrical pore model with diameter a and pore length L or LT if the tortuosity T is taken into account. The thickness of the lead sulfate layer is d_s . The radial current density through the lead sulfate layer is j_s and the density through the core cross section is j_p .

and lead sulfate production is high in this area. A thin layer of lead sulfate is formed at the orifice and the current can penetrate deeper into the pore. The result is that soon the whole surface of the pore is covered with a thin lead sulfate layer [19] and the voltage difference between the plate surface and the electrode connector becomes almost constant. The discharge then proceeds under constant voltage plateau conditions.

Once the inner surface is completely covered we can represent the pore by a conductor surrounded by a less conducting lead sulfate layer of thickness d_s . The radial conductance G_s of the lead sulfate layer and the longitudinal resistance R_a of the acid in the pore (Fig. 2) follow from:

$$G_s = \frac{\pi a L}{\rho_s d_s} \quad (1)$$

$$R_a = \rho_a \frac{4L}{\pi a^2} \quad (2)$$

The symbols ρ_a and ρ_s represent the specific resistances of the acid and lead sulfate layer, respectively. Alternately we will also use the acid conductance $\sigma_a = 1/\rho_a$. The corresponding longitudinal unit resistance r_a and radial surface conductance g_s per meter are:

$$g_s = \frac{\pi a}{\rho_s d_s} \quad (3)$$

$$r_a = \frac{4\rho_a}{\pi a^2} \quad (4)$$

As shown in Fig. 3, the pore can electrically be represented by a distributed resistor-conductor line. The potential outside the pore is supposed to be constant

and is taken as the zero reference. This is because of the acid and the conducting skeleton that surrounds the pore. If a constant discharge current I enters the pore at $x=0$ then, at the centre of the plate ($x=L$) we have $I=0$ since it is supposed that equal currents enter the left and the right side of the plate. For a half plate and by applying Kirchhoff's laws, we obtain the following differential equations for the voltage $v(x)$ and the current $i(x)$ of the continuous system:

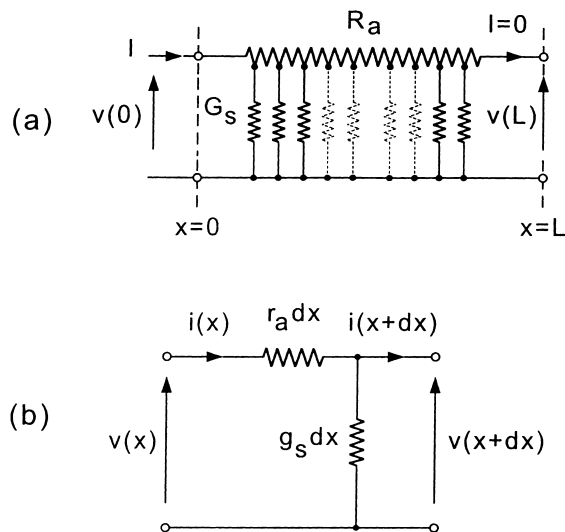


Fig. 3. Electrical equivalent circuit (a) of the pore with its distributed resistance R_a and lead sulfate conductance G_s . The potential outside the pore is taken as zero. In (b) the equivalent circuit of an elementary cell pore is shown. The unit length resistance of the pore acid and the unit length conductance of the lead sulfate layer on the pore surface are respectively r_a and g_s .

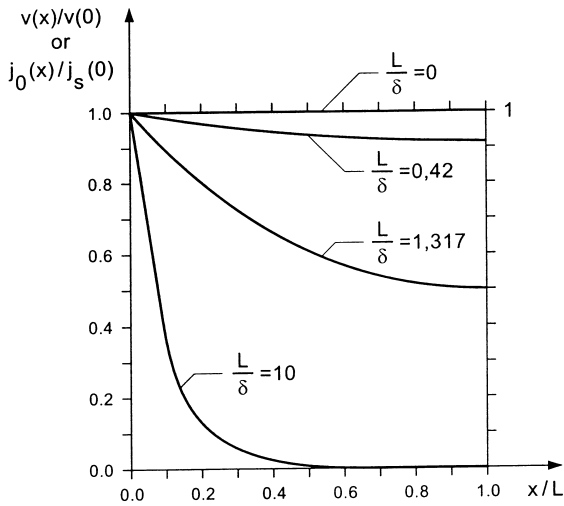


Fig. 4. Representation of $j_s(x)/j_s(0) = v(x)/v(0)$ for different parameter values $L/\delta = 0; 0.42; 1.317$ and 10 .

$$\frac{\partial^2 v(x)}{\partial x^2} - g_a r_s v(x) = 0, \quad \frac{\partial^2 i(x)}{\partial x^2} - g_a r_s i(x) = 0 \quad (5)$$

With the boundary conditions $i(0) = I$ and $i(L) = 0$, we obtain the solution:

$$v(x) = I \sqrt{\frac{r_a}{g_s}} \frac{\cosh \frac{L-x}{\delta}}{\sinh \frac{L}{\delta}} \quad (6)$$

$$i(x) = I \frac{\sinh \frac{L-x}{\delta}}{\sinh \frac{L}{\delta}} \quad (7)$$

$$\delta = \frac{1}{\sqrt{r_a g_s}} = \frac{1}{2} \sqrt{\frac{\rho_s d_s a}{\rho_a}} = \frac{1}{2} \sqrt{\rho_s d_s a \sigma_a} \quad (8)$$

At the entry of the pore ($x=0$) the equivalent input resistance $R = v(0)/i(0)$ becomes:

$$R = \sqrt{\frac{r_a}{g_s}} \coth L/\delta \quad (9)$$

The current flowing through the lead sulfate layer with conductance g_s will continue to generate lead sulfate and the corresponding current density j_s involved is, taking into account Fig. 3(b):

$$\begin{aligned} j_s &= \frac{-1}{\pi a} \frac{\partial i}{\partial x} = \sqrt{r_a g_s} \frac{I}{\pi a} \frac{\cosh \frac{L-x}{\delta}}{\sinh \frac{L}{\delta}} \\ &= \frac{I}{\pi a L} \frac{L}{\delta} \frac{\cosh \frac{L}{\delta} \left(1 - \frac{x}{L}\right)}{\sinh \frac{L}{\delta}} \end{aligned} \quad (10)$$

The value of the parameter δ which has the dimension of length can be estimated by using the values commonly found in literature, e.g. [12]: $\rho_s = 3.10^7 \Omega \text{m}$, $\rho_a = 1.2 \times 10^{-2} \Omega \text{m}$, $d_s = 0.03 \mu\text{m}$, $a = 0.3 \mu\text{m}$, $L = 10^{-3} \text{m}$. This gives with Eq. (8) a value $\delta = 2370 \mu\text{m}$ and thus $L/\delta = 0.42$ if we take $T = 1$. Fig. 4 shows the distributions along the length of the pore of $j_s(x)$ (Eq. (10)) and $v(x)$ (Eq. (6)), normalised with respect to their values at $x=0$ for $L/\delta = 0; 0.42; 1.317$ and 10 . With the calculated L/δ we see from Eq. (6) that the ratio $v(L)/v(0) = 0.918$ and at $x=L$ the voltage $v(L)$ is only 8.2% lower than $v(0)$. Therefore, it is admissible to approximate the functions in Eqs. (6)–(10) by the first terms of their series expansions:

$$v(x) \approx I \sqrt{r_a/g_s} \left[1 + \frac{1}{2} \left(\frac{L-x}{\delta} \right)^2 \dots \right] \quad (11)$$

$$i(x) \approx I \frac{\delta}{L} \left(\frac{L-x}{\delta} + \dots \right) \approx I \left(1 - \frac{x}{L} \right) \quad (12)$$

$$R \approx \frac{1}{g_s L} \quad (13)$$

$$j_s \approx \frac{I}{\pi a L} \quad (14)$$

The latter equation shows that the current density j_s is almost the same in every point of the internal pore surface once we operate at plateau voltage discharge conditions. This means that the rate of the lead sulfate production is also the same in every point of the pore surface at the quasi stationary conditions, during a discharge. One must realise that δ is not very sensitive to variations of the parameters in Eq. (8), due to the square root operation.

Further, we can see that at the beginning of the discharge the process is time dependent: at the start of the discharge the thickness d_s of the lead sulfate layer is zero and $v(x)$ is almost zero at every point of the pore since the acid is short circuited by the lead (or lead oxide) of the plate. The largest potential drop occurs at the orifice where the lead sulfate is generated. At that stage the current density $j_s(x)$ strongly depends on the position x . The increasing resistance of this

layer permits the current to penetrate further into the pore. The voltage in the pore builds up until it becomes nearly constant over the pore length. Eventually, the thickness of the lead sulfate layer tends to become nearly constant over the pore length. This is caused by the self regulating action of the sulfate production: if for some reason the thickness d_s becomes larger than the average value over the pore length in a point, the corresponding current density, and thus the rate of lead sulfate production, will locally decrease. From Eq. (8), since an increase of d_s is partially compensated by the corresponding decrease of pore diameter a , then δ remains nearly constant. This mechanism, and the absence of a sufficient longitudinal potential drop, is a possible explanation of the occurrence of flat lead sulfate levels over the pore length in the plate during a discharge. As long as current can flow in the pore this regulation process tends to equalise the thickness of the lead sulfate layer and the acid in the pore can be exhausted.

It remains to be determined at what conditions the pore acid is exhausted. The relation between conductivity σ_a and the acid concentration or the mass fraction w is well known. If we use e.g. the conductivity table given by Bode [12], then we can approximate σ_a by a parabola in the range $0 < w < 0.35$:

$$\sigma_a = 550w(1 - 1.67w) \quad (15)$$

with σ_a in S/m and w = mass H_2SO_4 /total mass of acid solution. Eq. (15) permits one to calculate w if σ_a is given without using a conductivity table. The parabola shows a maximum value for σ_a of 82 S/m at $w = 0.299$ or about 30% mass fraction.

Exhaustion of the pore is reflected in the current and voltage distributions and deviation from the simplified laws of Eqs. (11) and (14). From Eq. (10) we find the ratio of the radial current density at the centre of the plate and the current density at the entrance of the pore: $j_s(L)/j_s(0) = 1/\cosh(L/\delta)$. This equation permits one to calculate the acid concentration corresponding with a given amount of deviation from the ideal situation. We will allow the current density $j_s(L)$ at the centre of the plate to be an arbitrary fraction of the constant value predicted by Eq. (14). If we take e.g. as a limit this ratio equal to 50%, we obtain for δ the value $\delta = L/1.317$. From Eq. (8) we can calculate the corresponding minimum conductivity σ_a of the acid if appropriate values for the quantities ρ_s , d_s and a are introduced. With the values given above and for $a = 0.3 \mu\text{m}$ we obtain $\sigma_a = 8.54 \text{ S/m}$. Eq. (15) gives a corresponding mass fraction $w = 0.015$ or about 1.5%. For the larger macropores with $a = 3 \mu\text{m}$, this value will be further reduced with a factor of ten. As a matter of fact, the 50% limit corresponds with all parameter combinations a and σ_a that fulfil the equality

$a\sigma_a = 2.56 \times 10^{-6} \text{ S}$. Although a pore can be almost completely exhausted, a non-uniform radial current density $j_s(x)$ can still exist over the whole pore length. The unequal current distribution will, however, be counteracted by the self regulation mechanism of the lead sulfate layer growth. Finally, if the acid is completely depleted the voltage drop in the pore will be so large that no further discharge can occur at the centre of the plate (Fig. 4).

The important thing to remember is that even for very low acid concentrations ($w < 1.5\%$) in the pore a current density can still exist at the centre of the plate. If the mass fraction is further reduced, $a\sigma_a$ will fall below $2.56 \times 10^{-6} \text{ S}$. For example, with $L/\delta = 10$ corresponds $a\sigma_a = 0.044 \times 10^{-6} \text{ S}$ (Fig. 4) and we see that the centre of the plate is completely depleted, i.e. the concentration is zero. This is a valuable property because it will simplify the diffusion calculations of paragraph 3.2. Eqs. (1)–(10) are valid for all values of the discharge current and depth-of-discharge since they represent the behaviour of an electrical circuit. The parameters ρ_s , L , a and ρ_a are constant in a first approximation. The thickness d_s of the lead sulfate layer, however, changes with the depth-of-discharge. But, as long as $L/\delta \geq 1.317$, our former conclusions remain valid.

It can be remarked that if pore depletion occurs, the effective pore input resistance will increase while the plate discharge voltage decreases. This is unimportant since the discharge is performed at a constant current. On the other hand, several phenomena have been neglected in our model:

1. Shrinking of the pore section S and its perimeter P due to the lead sulfate production during a discharge.
2. Variation of d_s during the discharge.
3. Dependence of the shape of the lead sulfate crystals on the current density.
4. Influence of different kinds of lead sulfates.
5. Pore blocking and plate breathing.
6. Ion migration due to the potential drop along the x -axis and mass transport in the pore.
7. Differences between positive and negative plates.

Since most of the properties of Fig. 1 can be explained with our model, we may suppose that it represents a reasonable approximation of reality.

2.2. Diffusion in the pore

In the pore, acid will be replenished by an acid diffusion flow from the reservoir between the plates. The mass-flow equation describing the concentration $C(x, t)$ of the acid in the cylindrical pore at the point x follows from Fig. 5. As a result of the observations made

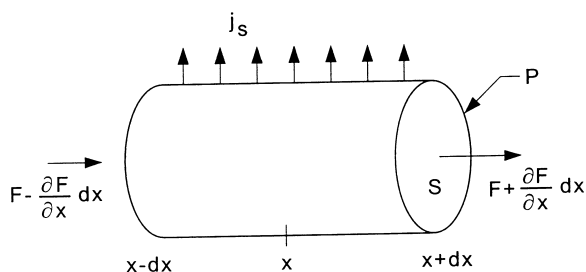


Fig. 5. Elementary cell for calculating the mass-flow F (in $\text{kg}/\text{m}^2 \text{ s}$) in $(x-dx, x+dx)$ through a pore cross section S .

in the previous section, we will exclude the start of the discharge and assume that the radial current density j_s through the lead sulfate layer is constant over the entire pore length. Every Coulomb discharged transforms 1.236 mg PbO_2 at the positive plate and 1.072 mg Pb at the negative plate into 1.57 mg PbSO_4 at both plates. The total quantity of material transformed within the elementary section $(-dx, +dx)$ is therefore equal to $2kj_sPdx$, with P the pore perimeter and the constant $k=1.57 \text{ mg/C}$. For a pore with a cross section of S we thus obtain the following mass-balance equation for the acid mass-flow F (in $\text{kg}/\text{m}^2 \text{ s}$):

$$-\frac{\partial F}{\partial x} S dx - kj_s P dx = \frac{\partial C}{\partial t} S dx \quad (16)$$

From Eq. (16) we can define the quantity A :

$$A = \frac{kj_s P}{S} \quad (17)$$

This quantity (dimension $\text{kg}/\text{m}^3 \text{ s}$), which represents the mass of transformed material per unit of time and volume, is constant due to our assumptions. Using Fick's first law ($F = -D \frac{\partial C}{\partial x}$), we introduce the diffusion constant D :

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - A \quad (18)$$

The radial current density j_s follows from the pore current density j_p perpendicular to the pore entrance at the orifice $x=0$:

$$j_s = \frac{j_p S}{PL} \quad (19)$$

The total current I_p of a cell is equal to j_p multiplied by the total pore cross section over the plate surface ΣS :

$$I_p = j_p \Sigma S \quad (20)$$

Eqs. (19) and (20), combined with Eq. (17), give:

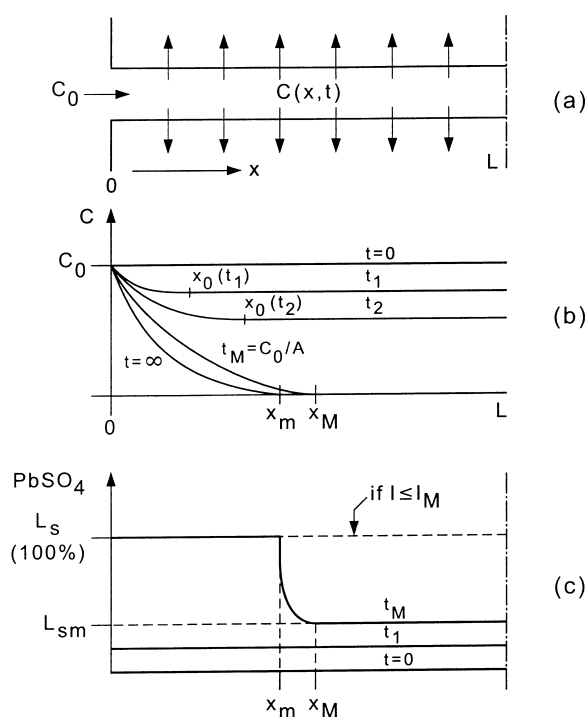


Fig. 6. Pore with a constant mass transformation at the surface (a), solution of the diffusion equation (b), lead sulfate levels resulting from this solution. At the time t_M the concentration becomes zero in the entire range (x_M, L) and the point x_M moves to the left until the steady-state position x_m is attained. The level 100% in (c) corresponds to the maximum lead sulfate content, whereby all the active material is transformed into lead sulfate.

$$A = \frac{kI_p}{L\Sigma S} \quad (21)$$

The fact that the current in the pore can flow at very low mass fraction means that Eq. (18) is valid everywhere in the pore as long as $C(x, t) > 0$, for $0 < x < L$ and all $t > 0$. A solution of Eq. (18) has to fulfil the following initial and boundary conditions:

$$C(0, t) = C_0 \quad (22)$$

$$C(x, 0) = C_0, \quad 0 < x < L \quad (23)$$

$$\frac{\partial C}{\partial x}(L, t) = 0 \quad (24)$$

The latter equation is due to the symmetry axis at the centre of the plate. Fig. 6 shows the lead sulfate evolution in a pore. As long as $C(L)$ is positive, the current density j_s in dx is independent on x and a constant amount of lead sulfate is produced. The acid concentration correspondingly decreases and this starts

the diffusion process. Initially (Fig. 6(b), $t=0$) the diffusion of acid is restricted to the pore orifice. At $t=t_1$ and in the range $(0, x_0)$, more acid diffuses from left to right than is consumed by the lead sulfate production. At the point x_0 the net flow of acid becomes zero:

$$\left. \frac{\partial C}{\partial x} \right|_{x=x_0} = 0 \quad (25)$$

For $x > x_0$ only the acid in the pore is available. We are thus able to find the exact solution of Eq. (18) by assuming that for all $x > x_0$, the acid concentration is independent on x . This means that all derivatives with respect to x are zero:

$$\frac{\partial C}{\partial x} = \frac{\partial^2 C}{\partial x^2} = \dots = 0$$

Since the radial current density j_s is constant, A is also constant and due to Eq. (18), the concentration in the range (x_0, L) will fall linearly in time:

$$C = C_0 - At, \quad x_0 \leq x \leq L \quad (26)$$

As a result, the boundary x_0 will gradually penetrate into the pore. For the range $(0, x_0)$ we can approximate the exact solution as follows. Due to Eq. (26) we have:

$$\left. \frac{\partial C}{\partial t} \right|_{x_0} = -A$$

and the rate of change of the concentration is zero at $x=0$ since $C(0)=C_0$, thus:

$$\left. \frac{\partial C}{\partial t} \right|_0 = 0$$

If we approximate the curve $\partial C/\partial t$ by a straight line in the interval $(0, x_0)$ then, with Eq. (18), we obtain:

$$\frac{\partial C}{\partial t} = -A \frac{x}{x_0} = -A + D \frac{\partial^2 C}{\partial x^2} \quad (27)$$

or:

$$\frac{\partial^2 C}{\partial x^2} = -\frac{Ax}{Dx_0} + \frac{A}{D} \quad (28)$$

As long as $C_0 - At$ remains positive, the current is uniformly distributed and A is constant. The solution of Eq. (28) with the conditions (22)–(25) becomes:

$$C = \frac{-A}{6D\sqrt{6Dt}} x^3 + \frac{A}{2D} x^2 - \frac{A}{2D} \sqrt{6Dt} x + C_0 \quad (29)$$

The concentration in the interval (x_0, L) becomes zero at the time $t_M = C_0/A$ and the corresponding end point $x_M (= x_0(t_M))$ follows from Eq. (29) with $C=0$. If this

condition is substituted in Eq. (29), we find an equation which determines x_M :

$$-\frac{A}{6DC_0} \sqrt{\frac{A}{6DC_0}} x_M^3 + \frac{A}{2DC_0} x_M^2 - \sqrt{\frac{3A}{2DC_0}} x_M + 1 = 0 \quad (30)$$

Introduction of a new variable $\bar{x} = x_M/\lambda$, wherein $\lambda = \sqrt{2DC_0/3A}$, transforms Eq. (30) into:

$$-\frac{\bar{x}^3}{27} + \frac{1}{3} \bar{x}^2 - \bar{x} + 1 = 0 \quad (31)$$

This equation has a triple root $\bar{x}=3$ or $x_M=3\lambda$, and thus:

$$x_M = \sqrt{\frac{6DC_0}{A}} = \sqrt{\frac{6DC_0 L \Sigma S}{kI_p}} \quad (32)$$

On the other hand, if we consider the steady-state solution for which $\partial C/\partial t=0$, then Eq. (18) simplifies to:

$$D \frac{\partial^2 C}{\partial x^2} = A \quad (33)$$

$$C(0) = C_0, \quad \left. \frac{\partial C}{\partial x} \right|_{x_m} = 0, \quad C(x_m) = 0 \quad (34)$$

With these conditions, the steady-state solution of Eq. (33) becomes:

$$C = \frac{A}{2D} (x - x_m)^2, \quad x_m = \sqrt{\frac{2DC_0}{A}} \quad (35)$$

But, in the steady-state situation, the current density is zero for $x_m \leq x \leq L$. It means that the radial current density in $(0, x_m)$ changes gradually from its value j_s given by Eq. (19) to a new equilibrium value $j_s = j_p S / P x_m$. The rate of mass transferred also changes abruptly from the constant value of Eq. (17) to $A = kI_p/x_m \Sigma S$, which becomes finally $A = kI_p/x_m \Sigma S$, once the steady-state is established. Therefore, the penetration depth x_m can be expressed as a function of the total pore current by means of Eq. (35), wherein the rate of mass transferred has to be replaced by the new value. From this we obtain:

$$x_m = \frac{2DC_0 \Sigma S}{kI_p} = \frac{2DC_0}{kj_p} \quad (36)$$

The ratio x_M/x_m follows from Eq. (32) and Eq. (36):

$$\frac{x_M}{x_m} = \sqrt{\frac{3kI_p L}{2DC_0 \Sigma S}} \quad (37)$$

Besides the phenomena mentioned at the end of para-

graph 2.1, the analysis here given takes not into account how the point x_M changes in time to its new value x_m . This can be studied with a computer simulation, but falls outside the scope of this article.

3. Results

We are now able to complete the picture of the events in Fig. 6 as follows. Initially, the concentration in the interval $(0, L)$ steadily falls from C_0 to zero and meanwhile a constant lead sulfate level is formed everywhere in the pore. From the time $t_M = C_0/A$ on, the acid is completely depleted in the range (x_M, L) . The transition point x_M then gradually moves to the left until it attains the steady-state position x_m . In the range $0 \leq x \leq x_m$, the lead sulfate layer can grow continuously and thus a flat level is obtained. The shape of the lead sulfate profile in the range (x_m, x_M) depends on the time it takes for the transition point to move from x_M to x_m . If this transition is fast enough then the profile will show a fast decay from left to right. After complete transformation of active material into lead sulfate, the lead sulfate content (in arbitrary units) is maximal in the range $(0, x_m)$ (Fig. 6(c)). This represents the 100% level in the figures of the lead sulfate distribution. If we neglect the contribution of the lead sulfate in the depletion and transition zones to the discharge, the discharge capacity Q is proportional to the area under the maximum lead sulfate level, i.e.:

$$Q = Kx_m = \frac{2KD_0}{kI_p} \Sigma S \quad (38)$$

It follows that the product QI_p is constant and this corresponds to an exponent $n=1$ in Peukert's law:

$$QI^n = \text{Constant} \quad (39)$$

It is also possible that the maximum lead sulfate level is reached after a short time and that the wall stops near x_M . Since x_M is proportional to $I_p^{-0.5}$, the Peukert exponent becomes 0.5 in this case. On the other hand, if the cell is slowly discharged, the acid in the pores is sufficiently replenished and Q will not depend on I_p , or $n=0$. Since the diffusion constant is as a first approximation proportional to the temperature, it follows from Eq. (39) that Q is also proportional to temperature. For a linearisation at room temperature (25°C), we find for the temperature θ^0 and with a temperature coefficient α_{25} :

$$QI = \text{Constant}[1 + \alpha_{25}(\theta^0 - 25)] \quad (40)$$

The transition between both modes of discharge occurs when x_m falls at $x=L$. The maximum current (I_M) and the corresponding plate current density J_{pM} that can

be taken from the cell, without decreasing the maximum capacity, are therefore:

$$I_M = \frac{2DC_0\Sigma S}{kL}, \quad J_{pM} = \frac{2DC_0}{kL} \quad (41)$$

Eqs. (40) and (41) cannot be applied without some corrections. First, the tortuosity T and porosity θ of the plate influence the effective diffusion constant and D has to be replaced by $D\theta/T$ ([12] p. 83). Since θ , T , $L=L'T$ and the total pore areas are different for positive and negative plates, the transition currents I_{M+} and I_{M-} of the positive and negative plate are also different. Their ratio follows from:

$$\frac{I_{M+}}{I_{M-}} = \frac{\theta_+}{\theta_-} \frac{\Sigma S_+}{\Sigma S_-} \frac{L_-}{L_+} \quad (42)$$

In a practical situation the exponent n in Peukert's equation is situated in the range $(0-1)$, whereas experimentally $n \approx 0.4$ is found [14].

The model also gives information about the minimum quantity of lead sulfate (L_{sm}) that is formed in the first phase in the range (x_m, L) . It suffices to calculate the amount of lead sulfate equivalent to the total amount of acid in this part of the pore. It is accepted that the electrical conduction of the acid becomes too low for material transformation when the internal acid concentration falls below 1 M ([12], p. 156). This observation does not take into account our considerations which are valid in the pore, wherein the concentration can be much lower. On the other hand, it can be seen from the lead sulfate distributions in the plates obtained by Bode et al. that the internal sulfate level is in an amount of about 25% of the maximum possible sulfate level. Thus, it is possible to correct Eq. (38) for this quantity:

$$Q = Kx_m + (L - x_m) \frac{K}{4} = \frac{3}{4} Kx_m + \frac{KL}{4} \quad (43)$$

This leads to the following capacity laws for the two modes of discharge:

$$\left(Q - \frac{KL}{4}\right)I = \text{constant}, \quad I \geq I_M \quad (44)$$

$$Q = KL, \quad I < I_M \quad (45)$$

These equations are an alternative to Peukert's law, but it has to be reminded that they are derived from the steady-state situation ($\partial C/\partial t = 0$) which at high discharge levels is not necessarily reached. Also, the lead sulfate in the transition zone (x_m, x_M) has been neglected. At last, it has been supposed that the acid concentration between the plates is constant. This is not

the case for starved electrolyte cells and in this case n can be much larger.

3.1. Radial diffusion in the pore

Although the former constant current density model explains the wall shaped structure of the lead sulfate level, it in no way gives account for the fact that the lead sulfate level in the zone (x_m, L) also varies with the discharge current. At large current density the level is lower than at a low current density, as can be seen in Fig. (1). In the above calculations it has been supposed that no acid gradient exists over the pore section. This means that the concentration over the pore section S is equalised almost instantaneously as is confirmed by the following consideration. For a cylinder with diameter a , which loses per second a constant amount A of material through its surface and which contains initially a concentration C_0 , the concentration $C(r)$ in a point at a distance r from the centre is given by Crank [15]:

$$C(r) = C_0 - \frac{Aa}{2D} \left[\frac{8Dt}{a^2} + \frac{2r^2}{a^2} - \frac{1}{4} - 2 \sum_{n=1}^{\infty} \frac{J_0\left(\frac{2r\alpha_n}{a}\right)}{\alpha_n^2 J_0(\alpha_n)} e^{-4D\alpha_n^2 t} \right] \quad (46)$$

$$-D \frac{\partial C}{\partial r} \bigg|_{r=a/2} = A, \quad C(r) = C_0 \quad \text{at} \quad t = 0 \quad (47)$$

The constants α_n are the roots of the Bessel function $J_1(\alpha)$. The exponential with the shortest time constant ($n=1$) in this solution has also the largest coefficient. For this reason it is possible to approximate Eq. (47) and calculate the concentration $C=C(a/2)$ at the pore surface:

$$C = C_0 - \frac{Aa}{2D} \left[\frac{8Dt}{a^2} + 0.25(1 - e^{-\frac{t}{\tau_1}}) \right] \quad (48)$$

$$\tau_1 = \frac{a^2}{4D\alpha_1^2}, \quad \alpha_1 = 3.83 \quad (49)$$

For the positive plate we have $a=0.5 \mu\text{m}$, $D=1.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and the time constant $\tau_1=3 \mu\text{s}$; for the negative plate $a=5 \mu\text{m}$ and $\tau_1=300 \mu\text{s}$. The conclusion is that the concentration redistributes almost immediately over the pore section and this mechanism can therefore not explain the current dependence of the central lead sulfate distribution.

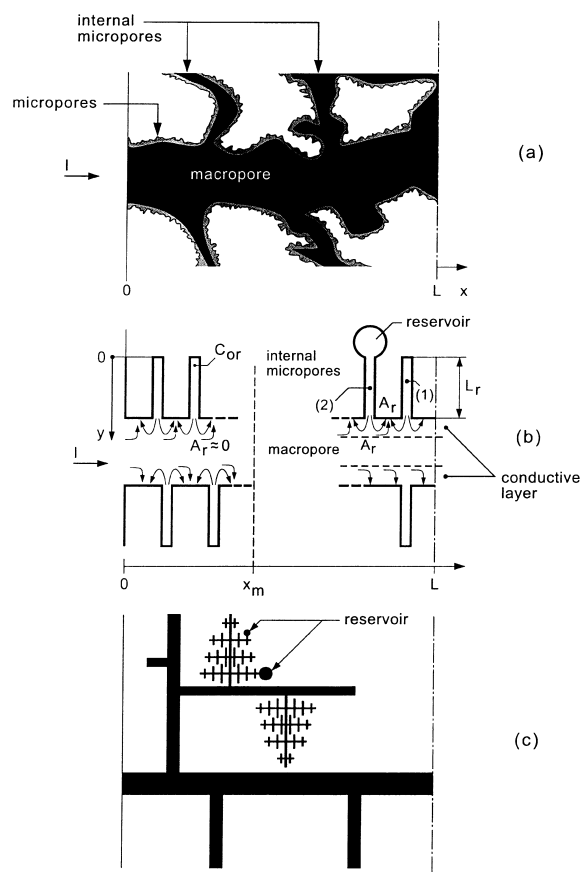


Fig. 7. Macropore with associated surface micropores and internal micropores (a), model of macropore extended with internal micropores and reservoir (b), possible fractal dendrite model (c). In the range (x_m, L) , the acid is transported by diffusion from the internal pore to the surface of the macropore and immediately consumed in a thin layer at the macropore surface. In the range $(0, x_m)$, only a small part of the acid comes from the internal pore since the acid concentration in the macropore is high in this range.

3.2. Secondary pores

The conjecture we make here, in order to explain the current density dependent lead sulfate distribution in the centre of the plates at high current densities, is that the large amount of acid which is fixed in cracks and voids between the macropores, and which represent the microporosity of a plate, plays a role in this situation. There exist a number of facts in favour of this idea.

First of all, from SEM pictures [12,20] it can be seen that the actual plate surface has a complicated cauliflowerlike structure with macropore entrances and micropores. During the formation process of a plate, macropores are formed with an *average* direction per-

pendicular to the plate surface (Fig. 7(a)). This is because the mass flow of the acid during a charge/discharge cycle is in average perpendicular to the plate surface. In a well formed plate the macropores serve also to penetrate the active mass as deeply as possible in order to permit a mass flow from the internal plate structure to the plate surface. The cylindrical pore model is only a crude representation of an average pore. In the descriptions of pore models it is explicitly [2,16] or implicitly [1] stated that the model pore is perpendicular to the surface in order to obtain a simple one- or two-dimensional model. The real shape of the pore is taken into account by multiplying the ideal geometrical pore length with the tortuosity factor T . From an electrical point of view this is allowable because the internal acid of the pore and the skeleton outside the pore are almost equipotential as shown before, except for very long pores. On the other hand, initially the pasted plate material is isotropic in every point of the paste. Therefore, the macropore surface is composed of micropores with no preferential direction, on which the electrochemical reactions can take place. At this point we will make a distinction between the micropores in the immediate vicinity of the macropore surface and the micropores outside this region which we will call 'internal micropores'. The former micropores will accept a large current density because they are almost in direct contact with the macropore acid. The internal micropores are also connected to the macropore because this is the main way for the acid transport. However, since the internal micropore forms a rather long acid path, its resistance will hinder the current and only a small part of the main current will be diverted to it. Most of the current in the macropore will be used for the transformation of micropore material in the vicinity of the macropore surface. Otherwise, it is by no means sure that such an internal micropore will contain conducting material at its surface. In such a case its acid content will not be consumed. Since the acid concentration in a plate varies between 4 and 1 molar during the discharge, there must exist a large number of undepleted acid reservoirs somewhere at all time.

For this reason, we propose to extend the classic pore model by means of regularly spaced cylindrical internal micropores, with length L_r and connected to the main pore (Fig. 7(b)). It is possible that the internal pores could better be represented by a fractal dendrite structure (Fig. 7(c)), but for the sake of simplicity we will use the model of Fig. 7(b). As a matter of fact, the dendrite model of Fig. 7(c) is comparable to the grain model used by some authors [6]. The important thing is that L_r can be rather long (say 1 or 2 mm) and that the internal micropore still contains a considerable amount of acid at the moment the macropore is exhausted in the zone (x_m, L) . Three main

reasons for the availability of acid in the internal micropores can be considered.

1. The pore can be connected to a larger crack or cavity which is itself not directly connected to a macropore.
2. The micropore can be isolated from the conducting skeleton by lead sulfate crystals in such a way that no current path to the conducting skeleton exists.
3. The small current density in the internal micropore can only form a small amount of lead sulfate and consequently a considerable quantity of acid remains available.

Such a situation can be modeled by means of e.g. a spherical reservoir at the end of an internal micropore as shown in Fig. 7(b). It should be very enlightening if the studies of Pavlov et al. [23] could be extended towards a more fundamental description of the three-dimensional plate morphology, although this seems not to be an obvious task at the moment. We will suppose that the acid concentration at the reaction surface of the macropore remains homogeneous due to the presence of a large number regularly spaced micropore orifices at this surface. In order to explain the current dependence of the central lead sulfate level, one has to accept that the diffusion rate of acid from the inner part of the reservoirs to the macropore is of the same order of the rate of diffusion from the space between the plates into the macropore. If the diffusion rate were much faster, the acid from the reservoirs and the internal micropores would immediately mix with the acid in the macropore and the only effect would be that apparently the macropore contains more acid than calculated from its volume. If the diffusion rate were too slow, then the normal diffusion from acid outside the plate into the macropore would be prevalent.

Initially, during a high current discharge, the acid in the macropore will be depleted in the range (x_m, L) following the description we gave in section 2.2. This is not the case for the acid in the reservoirs and dendrites of our model, although some acid consumption cannot be excluded. Below we will accept that the internal pore is only a diffusion channel and neglect the possible lead sulfate production in it.

So, when the acid concentration decreases in the range (x_m, L) of the macropore, the diffusion through the internal micropores gradually starts and eventually, when the diffusion of acid from outside the plate through the boundary x_m has stopped, a thin acid layer can exist at the surface of the macropore in the range (x_m, L) . The result is that a current density can also exist in the same range. This current density will have a value compatible with the diffusion of acid through the dendrites (Fig. 7(c)) or idealised micro-

pores (Fig. 7(b)) and the total current through the section x_m associated with it has to be rather small compared with the total current entering the macropore. If this were not the case, the amount of lead sulfate formed would be of the same order as in the case where the macropore was initially not exhausted and no distinction between these two situations should be visible. The electrical conditions of the circuit also have to be met. It is possible to extend the theory of section 2.1 for this case, but this would introduce new parameters such as the acid density in this layer and it is doubtful if significant quantitative results could be obtained with such an approach.

The fact that the central sulfate level in Fig. 1 is flat proves that the current density due to the second diffusion mechanism is constant in the entire range (x_m , L), but of course it can still change in time. The amount of lead sulfate formed will be proportional to this current density. If the plate discharge current is decreased, the central lead sulfate level will eventually become higher because more time is available for the secondary diffusion process. This means that the current dependence of the central level is in fact caused by the time dependent diffusion. We will take it for granted that a plate can be considered to be discharged when the lead sulfate level in the zone (0, x_m) reaches its maximum, due to the strong increase of the plate resistance.

In the following, we will consider two cases for the secondary diffusion mechanism.

1. The only source of acid is in the volume of the internal micropores (micropore (1) in Fig. 7(b)). In this case, the amount of acid available is limited by the pore volume and initial concentration.
2. The internal micropore is connected to a reservoir at its end which provides most of the acid (micropore (2) in Fig. 7(b)). For the moment, we consider a reservoir with an infinite volume so that the concentration remains constant at the side of the pore connected to it. In the real plate we can accept that both situations exist.

In the first case the solution of the diffusion equation for a cylindrical micropore (Fig. 7(b), (1)) with a length L_r and filled with acid of concentration C_{0r} at $t=0$ can be derived from the plane sheet diffusion. We will use the following boundary and initial conditions:

$$C(y) = C_{0r}, \quad 0 < y < L_r, \quad t = 0 \quad (50)$$

$$C(L) = 0, \quad \text{for all } t \quad (51)$$

The latter condition expresses the fact that the macropore is exhausted at $t=0$ and remains exhausted because all the acid from the internal pore is immediately consumed at the macropore surface. The first

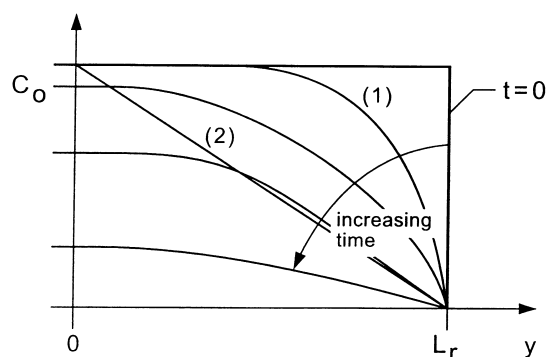


Fig. 8. Internal pore steady-state concentration with reservoir (1) and time dependent concentration without reservoir (2). The boundary condition is $C(L_r) = 0$.

condition is an idealisation since during the time the macropore acid concentration decreases, the internal pore concentration also decreases by diffusion to the macropore. The general solution for this case is found in [15] and the result is shown in Fig. 8:

$$C(x,t) = \frac{2C_{0r}}{\pi L_r} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-\frac{t}{\tau_n}} \cos \frac{(2n+1)\pi x}{2L_r} \quad (52)$$

$$\tau_n = \frac{4L_r^2}{(\pi)^2(2n+1)^2 D}, \quad n = 0, 1, 2, 3, \dots \quad (53)$$

The rate A_r of the acid flow at the orifice follows from $\partial C / \partial x$ for $x = L_r$. This gives the following equation:

$$\left. \frac{\partial C}{\partial x} \right|_{x=L_r} = \frac{-2C_{0r}}{L_r} \sum_{n=0}^{\infty} (-1)^n e^{-\frac{t}{\tau_n}} \quad (54)$$

The longest time constant involved is τ_1 and it will dominate after a short time. The rate of the acid flow therefore becomes:

$$A_r = \frac{2C_{0r}D}{L_r} e^{-\frac{t}{\tau_1}} \quad (55)$$

Since this acid rate is immediately transformed into lead sulfate by the current density in the conducting layer it is in principle possible to calculate this current density. The strong time dependence suggests that the current density varies exponentially in time and finally becomes almost zero after a sufficiently long time, e.g. when $t \geq 3\tau_1$. By substituting reasonable values in Eq. (53), the value of τ_1 can be estimated. For example, $D = 2 \cdot 10^{-9} \text{ m}^2 \text{ s}$, $L_r = 1 \text{ mm}$ or more. This gives $\tau_1 = 200 \text{ s}$. For a tortuosity $T = 3$, this rises to 1800 s or 30 min.

In the second case it is supposed that the dendrite or internal micropore forms the connection between a large reservoir and the macropore as in Fig. 7(b)(2), the concentration $C_{0r}(0)$ is almost zero due to the exhaustion of the macropore and the steady-state mass flow follows from the plane sheet diffusion equation with $C(L_r)=0$. The latter condition is acceptable if one is reminded that all sulfate ions are immediately transformed into lead sulfate in the micropore layer at the macropore surface. The steady-state concentration changes linearly between 0 and L_r and the maximum value of the acid mass-flow through the internal pore is: $A_r = DC_{0r}/L_r$. If the density of the internal micropore orifices could be known at the macropore surface, it should be possible to calculate from A_r the maximum total current passing through the boundary x_m . Of course, the current density in the range $(0, x_m)$ will lower somewhat due to this current but in principle, the value given by Eq. (36) could be corrected for this. If the current density is lower than the calculated one, diffusion can provide enough acid as long as the discharge criteria are not met, i.e. if the electrode potential remains at a sufficiently high value. This can readily be seen in Fig. 1 for the negative plate, whereby the central lead sulfate level at 90 mA/cm² has almost attained the steady-state value of the zone $(0, x_m)$. Since the first diffusion mechanism is limited due to the acid content of the internal pore, the second is probably the most important. The latter would imply an almost proportional increase of the central lead sulfate level in time. From the few experimental [3,12] lead sulfate distributions available, it is however impossible to deduce the exact time behaviour of the central lead sulfate level. The central level also contains the lead sulfate level L_{sm} of Fig. 6(c), which is due to the initial acid content of the macropore. A combination of both diffusion mechanisms is very likely to occur in the real situation.

4. Summary

The model described here gives a phenomenological explanation of Peukert's law. First it is shown that the potential drop in the pore in the longitudinal direction is relatively small because of the large acid conductance. From this it follows that a constant amount of material is transformed at the pore surface. The result is that the acid concentration in the pore decreases and diffusion from the reservoir between the plates starts. The model shows that for a sufficiently high current value, the inner part of the pore is depleted and takes no longer part in the discharge process. The diffusion equation then permits one to derive Peukert's capacity limiting law and most of the phenomena found by Bode et al. can at least qualitatively be explained.

Introduction of a second diffusion mechanism from internal acid reservoirs can explain the dependence of the central sulfate level on the current.

In the model we propose the discharge process proceeds as follows.

1. At low discharge rates, the conversion of active material into lead sulfate starts at the plate surface and the lead sulfate front penetrates into the pore until its entire internal surface is covered. Discharge can then proceed into the micropores at the surface of the macropore until all the acid in the macropore is transformed into lead sulfate. This is the 100% level of Fig. 6 and it corresponds with the ideal situation, i.e. $n=0$ in Peukert's law.
2. At high discharge rates, only the part of the pore near the plate surface is fed via diffusion from the acid reservoir between the plates and the 100% lead sulfate level can only be reached in this part. The acid in the inner part of the pore is depleted and used for the production of a constant amount of lead sulfate far below the 100% level. The exponent in Peukert's law is associated with the lead sulfate content of the wall: $n=1$ corresponds with a wall width x_m and $n=0.5$ with x_M . The fact that the lead sulfate level of the wall never reaches the level for the very slow discharge of Fig. 1 can be attributed to pore blocking, the shape of the lead sulfate crystals or the end-of-charge criterion used for the experiment.
3. If the main pore was the only source of sulfate ions, the lead sulfate level in the inner part of the pore would be constant. Since this is not the case, a second diffusion mechanism has been introduced. The single-pore model was extended by the addition of internal micropores. It is the acid in these micropores or in voids connected with it that is consumed when the main pores are depleted.

The model proposed here is suitable for cells with Planté or pasted plates with a large acid reservoir. For cells with low acid reserve and tubular plates it is expected to fail and one can assume that Peukert's law is also invalid in this case.

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